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(NII) NOVEL CATALYTIC, SYNTHESIS METHODS FOR MAIN GROUP

ROBERT BERGMAN
REGENTS OF THE UNIVERSITY OF CALIFORNIA THE

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14. ABSTRACT In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the β -diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes. We have since discovered that these well-defined niobium (III) complexes, in which low-valent Nb is stabilized by a labile arene ligand, are capable of activating fluoroaromatic substrates. The C-F activation shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for fluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene and fluorobenzene respectively. We have also been able to use these low-valent niobium systems to access niobium bis(imido) systems that are reactive across their metal-nitrogen pi-bonds. Recently, we have observed that these niobium bis(imido) complexes react reversibly with H ₂ and irreversibly with silanes via 1,2-addition. We have also observed that these bis(imido) compounds react with aryl isocyanides to exchange nitrene fragments between a tert-buty imido group and the isocyanide. DFT calculations suggest that this reaction proceeds through a [2+2]-like transition state.					
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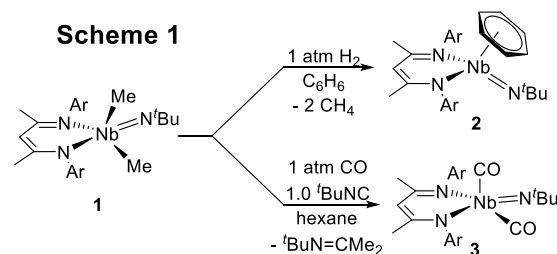
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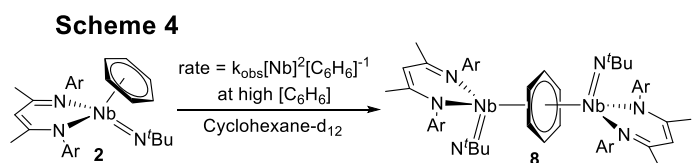
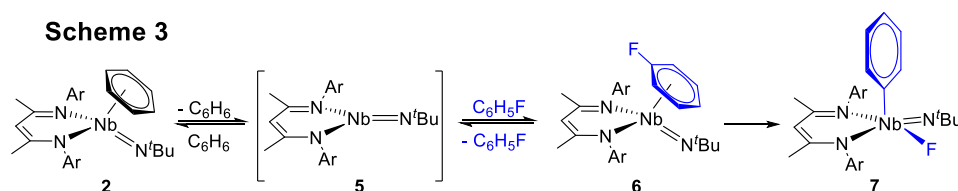
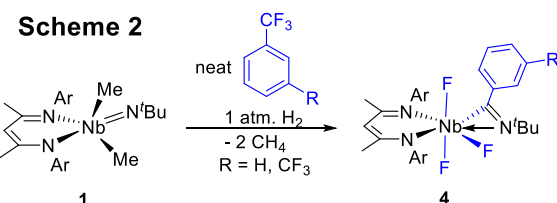
The following is a brief summary of the research results obtained as a result of support from the AFOSR. For a more exhaustive report of these results, please see our recent publications.

C-F Bond Activation with Low-Valent Niobium

Low-valent complexes of tantalum and niobium undergo a variety of unusual reactions with both organic and inorganic substrates. In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes (Scheme 1). These complexes have been shown to undergo a variety of interesting stoichiometric and catalytic reactivity, including activation of strong aromatic and benzylic carbon-fluorine and carbon-chlorine bonds.



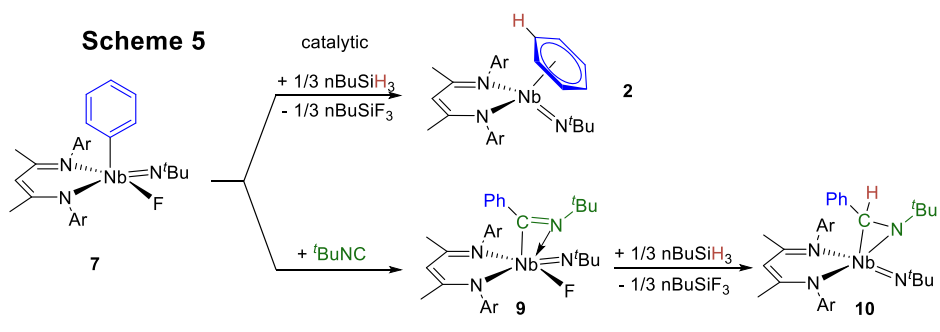
Within the past two decades, there has been a surge of interest in the activation of C-X bonds ($\text{X} = \text{F}, \text{Cl}$) by transition-metal complexes aimed at both waste removal and synthetic applications. In addition to waste remediation, activation of C-F and C-Cl bonds can be applied in selective functionalization of organic molecules. In recent chemistry relevant to this problem, we reported remarkable reactivity leading to dis-assembly of benzylic CF_3 groups via triple C-F bond activation (Scheme 2) that proceeds through a Nb(III) η^6 -arene intermediate. We have since discovered that the well-defined niobium (III) complex **2**, in which low-valent Nb is stabilized by a labile arene ligand, is capable of activating fluoroaromatic substrates (Scheme 3). Dissociation of the coordinated arene from **2** occurs readily at room temperature leading to the formation of a three-coordinate transient intermediate, **5**. Fluorobenzene then coordinates to give **6**, which undergoes C-F activation to form the aryl fluoride niobium (V) compound **7**. In this system, **6** appears to be a key intermediate for the C-F activation step since non-aromatic fluorinated species do not undergo C-F activation.



The C-F activation observed leading to complex **7** shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. We found that the niobium metal center is

highly reactive with the C-F bonds of fluorobenzene, difluorobenzenes, and some trifluorobenzenes, but does not react with pentafluorobenzene or hexafluorobenzene to any appreciable extent. In stark contrast, electron-rich late metals (i.e. group 7-10) tend to react preferentially with highly fluorinated arenes (e.g. C₆F₆), which have more highly polarized C-F bonds. DFT calculations suggest that the mechanism of C-F oxidative addition to complex **6** goes through a bimetallic transition state leading to an intermediate analogous to compound **8** (Scheme 4). These binuclear species may help to explain the unusual selectivity observed in this system in relation to the few examples of other transition metal systems that oxidatively add C-F bonds.

We have found that treating complex **7** with *n*-butylsilane results in H/F exchange, followed by reductive elimination of the hydrodefluorinated



arene (Scheme 5, top). Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for fluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene or fluorobenzene respectively. In the case of the difluorobenzenes, further catalytic hydrodefluorination to benzene occurs, but at a significantly slower rate, indicating that we may be able to use **7** to selectively functionalize only a single C-F bond in polyfluoroaromatics. We have also observed that treating complex **7** with *tert*-butyl isocyanide (Scheme 5, bottom) leads to the clean and rapid ($t_{1/2} \sim 2$ min) formation of the insertion product, complex **9**. This reacts with silane (PhSiH₃ or ⁿBuSiH₃) resulting in an H/F exchange and reductive elimination similar to that observed in the hydrodefluorination transformation, leading to the formation of an imine bound species **10**.

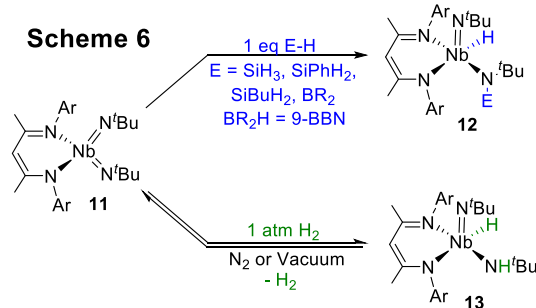
Reactivity across M-N π -bonds in Niobium Bisimido Complexes

We are interested in designing systems containing very reactive metal-ligand π bonds in the hope of activating a range of C-H bonds, as well as heteroatom-hydrogen (E-H) bonds (i.e. B-H, Si-H, N-H, and P-H) under mild conditions with the eventual goals of functionalizing chemical feedstocks and carrying out dehydrocoupling reactions to prepare useful materials and materials precursors. In addition to activating C-H and E-H bonds, we also are interested in using [2+2] and [3+2] reactions across metal imido bonds in order to functionalize unsaturated hydrocarbon substrates.

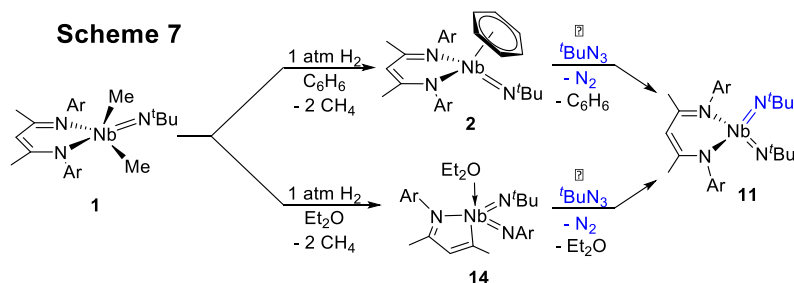
Recently, we have observed that the niobium bis(imido) complex **11** supported by a bulky BDI ligand also reacts reversibly with H₂ via 1,2-addition (Scheme 6). In this case, the equilibrium favors the hydrogenated product under reasonable pressures of H₂, allowing its

isolation and full characterization. **11** also reacts irreversibly with boranes and silanes via 1,2-addition to give borylamido and silylamido hydride species **13**. We are continuing to investigate the activation of other E-H bonds across the imido group, and are working toward utilizing these 1,2-additions to carry out processes such as dehydrocoupling.

Scheme 6



Two routes we have used to prepare **11** are shown in Scheme 7. The more direct route involves transfer of a nitrene group from an azide to a low-valent Nb fragment (Scheme 7, top).



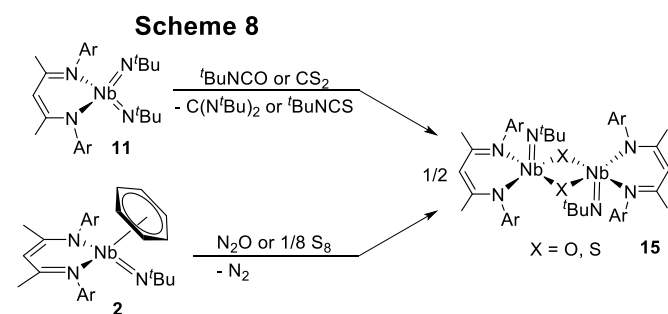
In the second route, hydrogenolysis of **1** in diethyl ether first results in transfer of a nitrene fragment from the BDI ligand to the niobium center via intramolecular reductive C-N cleavage to give the monoazabutadiene (MAD)

supported niobium bis(imido) complex **14** (Scheme 7, bottom). Interestingly, the BDI backbone can then be regenerated via reaction with *tert*-butylazide, thus demonstrating that like **2**, the niobium 5 complex **14** can act as a source of low-coordinate BDINb(N^{*t*}Bu).

Our studies have shown that generation of **11** from **14** proceeds through a tetrazine-type intermediate formed from [3+2] cycloaddition of *tert*-butylazide.

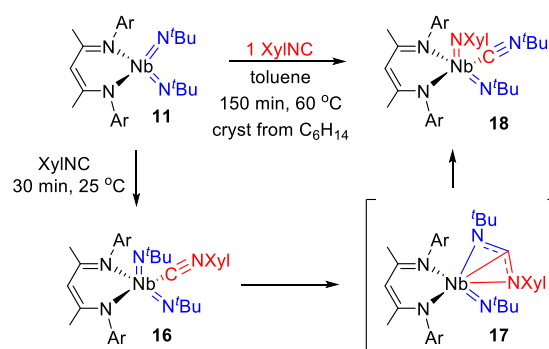
Compound **14** has also been shown to undergo [2+2] cycloaddition reactions with alkynes and strained olefins, clearly demonstrating that it is reactive across its Nb-N π -bonds.

We have observed that treatment of **11** with either *tert*-butylisocyanate or carbon disulfide results in generation of a bis- μ -oxo or bis- μ -sulfido product, respectively, which presumably result from dimerization of an initially generated terminal oxo-imido or sulfido-imido complex generated from [2+2] processes (Scheme 8, top). The same compounds are accessed through reaction of **2** or in-situ generated Nb(III) with oxygen or sulfur oxidants (Scheme 8, bottom). We have also observed that compound **11** reacts with 2,6-dimethylphenyl isocyanide (XylNC) to give compound **18**, which results from exchange of nitrene fragments between an imido group and the isocyanide (Scheme 9). DFT calculations suggest that this reaction proceeds through a [2+2]-like transition state to give an intermediate that resembles a reduced carbodiimide, then undergoes a



retro [2+2] reaction to give the product. Kinetic and mechanistic studies on this unusual reaction are ongoing.

Scheme 9



1.

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Abstract

In our efforts to develop reactive group 5 systems, we discovered that the combination of an imido group and the β -diketiminate (BDI) ligand provides a robust platform to support low-valent niobium complexes. We have since discovered that these well-defined niobium (III) complexes, in which low-valent Nb is stabilized by a labile arene ligand, are capable of activating fluoroaromatic substrates. The C-F activation shows unusual substrate selectivity in comparison with late transition metal compounds that activate C-F bonds. Under appropriate conditions, this hydrodefluorination reaction has been rendered catalytic for fluorobenzene, as well as for 1,2- and 1,3-difluorobenzene, releasing benzene and fluorobenzene respectively.

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Archival Publications (published) during reporting period:

1. Obenhuber, A. H.; Gianetti, T. L.; Bergman, R. G.; Arnold, J. "Regioselective [2+2] and [4+2] Cycloaddition Reactivity in an Asymmetric Niobium(bisimido) Moiety towards Unsaturated Organic Molecules." Chem. Commun. 2014.
2. Camp, C.; Maron, L.; Bergman, R. G.; Arnold, J. "Activation of White Phosphorus by Low-Valent Group 5 Complexes: Formation and Reactivity of Cydo-P4 Inverted Sandwich Compounds." J. Am. Chem. Soc. 2014.
3. Gianetti, T. L.; Nocton, G.; Minasian, S. G.; Kaltsoyannis, N.; Kilcoyne, A. L. D.; Kozimor, S. A.; Shuh, D. K.; Tylliszczak, T.; Bergman, R. G.; Arnold, J. "Electron Localization in a Mixed-Valence Dinioobium Benzene Complex." Chem. Sci. 2014.
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Changes in research objectives (if any):

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